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LOW-COST SOLAR ARRAY PROJECT

TASK I SILICON MATERIAL

"Investigation of the Hydrogenation of $SiCl_4$"

THIRD QUARTERLY REPORT

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ABSTRACT

A laboratory stainless steel reactor has been constructed and installed to study the hydrogenation of $SiCl_4$,

$$3\ SiCl_4 + 2\ H_2 + Si \rightleftarrows 4\ SiHCl_3$$

The reactor is designed to operate at pressure up to 500 psig which is the proposed operating pressure range of the Union Carbide EPSDU; silane-to-silicon process.

Series of experiments were carred out to measure the reaction kinetics. The effect of reactor temperature on the rate of the hydrogenation of $SiCl_4$ to $SiHCl_3$ was measured at 400°, 450°, 500° and 550°C. As expected, the reaction rate increases rapidly with increasing reactor temperature. The reaction rate and $SiHCl_3$ conversion were studied as functions of hydrogen and $SiCl_4$ concentrations at $H_2/SiCl_4$ ratios of 1.0 and 2.8. Higher $H_2/SiCl_4$ ratio produces a higher $SiHCl_3$ conversion per pass while the reaction rate remains approximately the same. The effect of reactor pressure on the rate of the hydrogenation reaction is most interesting. The rate of approaching equilibrium at higher reactor pressure (500 psig) is somewhat slower than those at lower reactor pressure (300 psig). In general, the 500 psig experimental data confirm previous estimated results which were obtained by extrapolating from lower reactor pressure data. Results of these experimental data show that the highest product $SiHCl_3$ output for a given reactor size is achievable by operating the hydrogenation process at maximum reactor temperature and pressure.

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INTRODUCTION

Work on the JPL Government Contract No. 955 382 began in April of 1979 to study the hydrogenation of $SiCl_4$ to $SiHCl_3$. This report is the third Quarterly Report in the series. Activities during this quarter include hydrogenation experiments to collect reaction kinetic data as functions of temperature, pressure and $H_2/SiCl_4$ ratio. As the first Milestone Check Point is reached, the Program Plan is reviewed and recommendations to JPL are made.

DISCUSSION

The laboratory scale stainless steel reactor for the hydrogenation of $SiCl_4$ is schematically shown in Figure I. The design and function of the hydrogenation apparatus were reported in detail in the first Quarterly Report (DOE/JPL 955 382 - 79/1). After starting up the hydrogenation reactor successfully, series of experiments were carried out to measure the reaction kinetics as functions of reactor temperature, pressure and $H_2/SiCl_4$ feed ratios. Results of these experiments are discussed in the following.

A. Reaction Kinetic Measurements

The hydrogenation reactor is designed to operate at pressures up to 500 psig. Since the hydrogenation of $SiCl_4$ to $SiHCl_3$

$$3\ SiCl_4 + 2\ H_2 + Si \rightleftarrows 4\ SiHCl_3 \qquad (1)$$

resulted in a net volume contraction as product $SiHCl_3$ is produced, higher reactor pressure will produce a higher conversion to $SiHCl_3$ as the equilibrium reaction (1) is driven to the right hand side.

The 500 psig pressure is also the proposed operating pressure range for the EPSDU of the Union Carbide silane-to-silicon process. The rate of the hydrogenation reaction is followed by measuring the rate of product formation as functions of varying reaction time. The reaction product mixture is analyzed by the in-line gas chromatograph which is schematically shown in Figure I. The only significant products produced in the hydrogenation reaction are dichlorosilane, SiH_2Cl_2, and trichlorosilane, $SiHCl_3$, plus unreacted $SiCl_4$. The reaction time is varied by gradually increasing or decreasing the $H_2/SiCl_4$ feedrate. In each measurement, gas chromatographic analyses of the reaction mixture are recorded until a duplicated analysis agrees within $\pm$ 1%. The reaction time is measured as residence time which is based on the movement of the inlet gaseous mixture passing through an empty reactor tube with a volume equal to the volume of the Si mass bed. The volume of the Si mass bed is defined as the weight of the 65 x 150 mesh (210 x 105 nm) Si mass divided by its bulk density of 1.2. For example, if the feedrate of the $H_2/SiCl_4$ gaseous mixture under the experimental condition is 100 c.c. per minute, the residence time is calculated to be 60 seconds with a 120 g Si mass bed in the hydrogenation reactor. The residence time as defined is a hypothetical number which provides a convenient common denominator for the reaction time measurements and to simplify the treatment of experimental rate data. In other words, parameters which influence the gaseous flow through the Si mass bed are neglected for the time being. These parameters may include particle size distribution (void space in the mass bed), volume contraction as $SiHCl_3$ is

produced (equation 1), bed expansion due to gas bubbles (fluidization mode), etc. These time-dependent parameters will be the subject of studies in later part of the Program Plan. At the end of each experiment, a mass balance is made to calculate the Si metal consumed by the hydrogenation reaction at each of the kinetic measurements. The residence time is then corrected by normalizing the weight of the Si mass bed to a constant value at the start of the experiment.

(1) Function of Temperature

A series of experiments was carried out to study the effect of temperature on the reaction rate at reactor pressure of 500 psig and $H_2/SiCl_4$ ratio of 2.8. Table I summarizes the reaction rate measurement at 500°C. Data in Table I are also shown in Figure II by plotting the percent $SiHCl_3$ conversion in Table I versus the residence time. The small amount of SiH_2Cl_2 by-product is neglected for the time being to simplify the data analyses. The hydrogenation experiment was repeated at 450°C and at 550°C. Results are summarized in Table II (450°C) and Table III (550°C) respectively. Data in Table II and Table III are also plotted in the same graph for the 500°C experiment in Figure II. The large effect of temperature on the $SiHCl_3$ conversion is clearly shown in Figure II. As expected, the reaction rate increases rapidly with increasing reactor temperature. Here, the reaction rate is defined as the rate at which the $SiHCl_3$ conversion approaches its equilibrium value.

As shown in Figure II, the plots at 450°C and at 550°C show a smooth curve. The graph for these two temperatures represent

single tests carried out for short periods of time within one day. On the other hand, the plot at 500°C represents a collection of separated experiments with a Si mass bed at various stages of conversion. The scattering of data points at 500°C is most likely due to the effects of other time-dependent parameters yet to be determined. For example, as the Si metal is consumed in the hydrogenation reaction, the total solid surface area varies and the particle size distribution changes. Also, as Si is consumed, impurities in the m.g. grade silicon metal are released and their effect on the reaction rate is not known at the present time. The solid circles in the 500°C plot are data points collected with a fresh Si mass bed. On the other hand, the partially shaded circles in the 500°C plot represent data points collected with a partially converted Si mass bed (15% to 25% conversion). The scattering data points in the 500°C experiment is significant but it is much smaller in comparison with the effect of temperature. These experimental results suggest that while the effects of these time-dependent parameters on the reaction rate are significant, apparently, they are not very large. The effect of surface area, particle size distribution and impurities are subjects of investigation which will be carried out later on in the Program Plan.

Another series of experiments was carried out to study the effect of temperature on the reaction rates at 300 psig and $H_2/SiCl_4$ ratio of 1.0. Results of these experiments are summarized in Table IV (550°C), Table V (500°C), Table VI (450°C) and Table VII (400°C). Data in these tables are also plotted in Figure III. Interestingly, at temperature as low as 400°C, the hydrogenation

of $SiCl_4$ to $SiHCl_3$ proceeds at a respectable rate. Again, these experimental data show the large effect of temperature on the reaction rate. Furthermore, the higher reaction temperature not only produces a faster reaction but also it gives a higher $SiHCl_3$ conversion even though the hydrogenation reaction is far from reaching equilibrium. This dramatic effect of temperature can be seen in Figure III. For example, at 60 seconds residence time, the hydrogenation of $SiCl_4$ at 550°C produces 31% $SiHCl_3$ while only 12% $SiHCl_3$ conversion is achieved at 400°C under the same experimental conditions.

(2) Function of $H_2/SiCl_4$ Ratio

Another series of experiments was carried out to study the effect of $H_2/SiCl_4$ concentration on the reaction rate at 300 psig with a $H_2/SiCl_4$ ratio of 2.8. The reaction was studied at reaction temperature of 500°C, 450°and 400°C,respectively. Results of these experiments are summarized in Table VIII (500°C), Table IX (450°C) and Table X (400°C). Data in these tables are also plotted in Figure IV. Under the same experimental conditions,the conversion to $SiHCl_3$ is significantly higher with a 2.8 $H_2/SiCl_4$ ratio (Figure IV) than those with a 1.0 $H_2/SiCl_4$ ratio (Figure III). The effect of $H_2/SiCl_4$ ratio on the hydrogenation reaction can be more clearly seen in Figure V by plotting one set of the 2.8 and 1.0 ratio data in the same graph. The higher $SiHCl_3$ conversion at a higher $H_2/SiCl_4$ ratio is expected. Since the formation of $SiHCl_3$ consumes hydrogen gas,

$$3\ SiCl_4 + 2\ H_2 + Si \rightleftarrows 4\ SiHCl_3$$

an increase in hydrogen concentration will drive the equilibrium reaction to the right hand side. The profile of these two kinetic curves in Figure V is very similar. Hence, the reaction rates, i.e., the rate at which the $SiHCl_3$ conversion reaches its equilibrium value, are not significantly effected by varying the $H_2/SiCl_4$ ratios in the feed.

(3) Function of Pressure

The effect of reactor pressure on the hydrogenation of $SiCl_4$ can be seen by comparing the kinetic data obtained at 500 psig (Figure II) with those obtained at 300 psig (Figure IV). This can be more easily observed by plotting these two sets of kinetic data in the same graph. For example, Figure VI shows the effect of reactor pressure on the reaction rates obtained under the same reaction temperature, 450°C, and $H_2/SiCl_4$ ratio of 2.8; but at a different reactor pressure of 500 psig and 300 psig, respectively. The effect of reactor pressure on the rate of the hydrogenation of $SiCl_4$ to $SiHCl_3$ is most interesting. As shown in Figure VI, the rate of approaching equilibrium is somewhat slower at 500 psig than than at 300 psig. At residence time shorter than 120 seconds, the conversion to $SiHCl_3$ is actually higher at 300 psig than those at a higher reactor pressure of 500 psig. With residence time longer than 120 seconds, the conversion of $SiCl_4$ to $SiHCl_3$ becomes higher than those at 300 psig. This is expected since the formation of product $SiHCl_3$ is thermodynamically more favorable at higher reactor pressure. However, it should be noted that this thermodynamic property applies to equilibrium conditions and it bears no relationship to reaction kinetics. The small but measureable differences

in the reaction rate between 500 psig and 300 psig suggest some mass action effect on the silicon metal surfaces. This phenomenon will be investigated later on in the reaction mechanism studies. Similarly, Figure VII shows the same effect of reactor pressure on the reaction rate but at a different reaction temperature of 500°C.

Although the reaction rate at 500 psig is somewhat slower at 500psig than that at 300 psig, the production rate in terms of pounds per hour of product $SiHCl_3$ is still much greater at higher reactor pressure. The mass throughput of a given reactor size is increased by 64% when the reactor pressure is raised from 300 psig to 500 psig. At 120 seconds residence time, a reactor which produces 1000 lbs/hr of $SiHCl_3$ at 300 psig will make about 1630 lbs/hr of $SiHCl_3$ when it operates at 500 psig instead. At 60 seconds residence time, the slower reaction rate at 500 psig gives 30% $SiHCl_3$ while 32% $SiHCl_3$ conversion is achievable at 300 psig. Although the reaction rate is slower, the production rate for $SiHCl_3$ (1530 lbs/hr) at 500 psig is still much higher than that at 300 psig; assuming that the reactor (a different one) is making 1000 lbs/hr of $SiHCl_3$ at 300 psig.

In summary, the effects of reaction temperature and reactor pressure are the most important parameters for the hydrogenation of $SiCl_4$ to $SiHCl_3$. Higher reaction temperature not only gives a faster reaction rate but also it produces a higher conversion to $SiHCl_3$. Similarly, higher reactor pressure not only gives a higher production rate with a given reactor size but also it produces a higher conversion to $SiHCl_3$ if one operates the hydrogenation process close to equilibrium conditions. In conclusion, maximum

reaction temperature and maximum reactor pressure produce the highest conversion of $SiCl_4$ to $SiHCl_3$. In other words, if one wants to maximize the output of $SiHCl_3$ with a given reactor size, one may achieve this by running the hydrogenation process at the highest practical reaction temperature and reactor pressure.

B. Equilibrium Constants

Earlier attempts (see last Quarterly Report DOE/JPL - 955 382 - 79/2) to measure the equilibrium constants for the hydrogenation of $SiCl_4$ showed that the reaction approaches equilibrium slowly. The hydrogenation reactor is a fluidized-bed design and it is not suitable for very long residence time studies. On the other hand, a sealed, static bed reactor is more suitable for these equilibrium constant measurements. A sealed reactor design is schematically shown in Figure VIII. The sealed reactor is used to replace the fluidized-bed reactor in the existing hydrogenation apparatus. A dip tube extending from the top of the reactor to the mid-point of the Si mass bed provides a sampling outlet for the equilibrium product composition measurements. It is connected directly to the existing in-line gas chromatograph. Construction and installation of the sealed, static bed reactor have been completed.

Equilibrium constant measurement for the hydrogenation reaction is not only a theoretical interest. The true equilibrium conversions of $SiHCl_3$ are essential data to establish a kinetic rate equation for the hydrogenation reaction. Variation of the equilibrium constants as functions of temperature provides useful thermodynamic data such as the free energy of reaction, ΔG, and the heat of reaction, ΔH.

C. Summary of Progress

Experimental work on the hydrogenation studies has progressed on schedule according to the attached Program Plan. During this third quarter, reaction rates for the hydrogenation of $SiCl_4$ to $SiHCl_3$ have been studied as functions of temperature (400°, 450°, 500° and 550°C), pressure (500 psig and 300 psig) with $H_2/SiCl_4$ ratios of 1.0 and 2.8, respectively. These new experimental results provide accurate reaction rate data for the hydrogenation of $SiCl_4$ and they generally confirm the previous estimates made for the EPSDUof the Union Carbide silane-to-silicon process. A sealed, static bed reactor has been constructed and installed for equilibrium constants measurements. Pressure and leak tests on this reactor were completed for preliminary experiments.

RECOMMENDATION

The first Milestone Check Point is reached after the reaction kinetic studies as shown in the Program Plan. Based on these new experimental data, the overall Program Plan is reviewed and recommendations to JPL are made.

(1) Experimental rate data show that temperature and pressure have the greatest and the most beneficial effect on the hydrogenation of $SiCl_4$ to $SiHCl_3$. One may achieve maximum product $SiHCl_3$ output by operating the process at the highest practical temperature and pressure.

(2) The reaction kinetic data collected at 500 psig generally confirm the previous estimates made for the EPSDU of the Union Carbide silane-to-silicon process. In fact, these new experimental

data show that one can achieve a somewhat higher conversion of $SiCl_4$ to $SiHCl_3$ than those estimated for the EPSDU.

(3) The in-line gas chromotograph arrangement allows an accurate measurement of the by-product dichlorosilane, SiH_2Cl_2. The 1% to 2% SiH_2Cl_2 conversion is significant, since it takes two moles of $SiHCl_3$ to make one mole of SiH_2Cl_2. Recovery of this by-product will further improve the efficiency of the hydrogenation process.

(4) The long residence time required for the hydrogenation reaction to reach equilibrium is unexpected. Since useful thermodynamic data can be derived from equilibrium constant measurements, experiments designed to collect these data are recommended. These experiments can be carried out concurrently with the copper catalyst studies planned for the next quarter without adversely effecting the overall Program Plan.

(5) As suggested by Union Carbide, a thin strip of Incoloy 800 test sample can be fixed at the inner side-wall of the hydrogenation reactor. This corrosion test is not intended for quantitative studies, such as corrosion rate measurements. Rather, it is a simple test to check if a significant corrosion problem exists. The small test sample does not significantly effect the reactor geometry. This corrosion test can be carried out concurrently with the planned hydrogenation experiments and it does not require additional effort in the Program Plan to carry out.

(6) The new experimental data on the reaction kinetic measurement show that the hydrogenation reaction is well-behaved and it can be easily controlled. There were no serious difficulties experienced with the hydrogenation experiments. It is recommended that the experimental work outlined in the Program Plan can be carried out as scheduled without any changes.

PROJECTED FOURTH QUARTER ACTIVITES

Planned activities for the fourth quarter (January - March) include:

- Continue hydrogenation experiments,
- Collect equilibrium data as functions of temperature,
- Calculate thermodynamic functions and establish a rate equation for the hydrogenation of $SiCl_4$ to $SiHCl_3$,
- Copper catalyst studies

TABLE I HYDROGENATION OF $SiCl_4$ AT 500 PSIG, 500°C AND $H_2/SiCl_4$ RATIO 2.8

Experiment No.	Hydrogen Feedrate SCCM(1)	Residence Time Second	Reaction Product Composition(2) mole% SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1A	4088	22.2	0.469	21.96	77.58
2A	2717	33.4	0.556	24.44	75.00
3A	2203	41.2	0.764	26.99	72.25
4A	1388	65.4	0.954	29.47	69.58
1B	1290	65.3	1.19	32.19	66.63
2B	925	91.1	1.29	33.36	65.36
3B	720	117	1.39	34.04	64.57
1C	662	117	1.55	35.04	63.41
D	470	193	1.52	35.42	63.06
4B	393	215	1.40	35.62	62.94
2C	345	224	1.74	37.12	61.14
3C	180	429	1.89	38.45	59.67

(1) SCCM Standard C.C. per minute

(2) Average of two or three analyses

TABLE II HYDROGENATION OF $SiCl_4$ AT 500 PSIG, 450°C AND $H_2/SiCl_4$ RATIO OF 2.8

Experiment No.	Hydrogen Feedrate SCCM(1)	Residence Time Second	Reaction Product Composition(2) mole% SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	2920	20.7	<0.05	12.54	87.48
2	2045	29.6	0.064	15.87	84.06
3	1675	36.1	0.140	17.60	82.29
4	1530	42.1	0.232	18.99	80.89
5	1215	53.0	0.393	21.15	78.46
6	1020	63.1	0.651	22.75	76.60
7	477	135	0.969	29.83	69.20
8	235	257	1.224	33.38	65.40

(1) SCCM, Standard C.C. per minute

(2) Average of two or three analyses

TABLE III HYDROGENATION OF $SiCl_4$ AT 500 PSIG, 550°C AND $H_2/SiCl_4$ RATIO OF 2.8

Experiment No.	Hydrogen Feedrate SCCM	Residence Time Second	Reaction Product Composition mole% SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	2948	17.7	0.770	28.49	70.74
			0.807	28.44	70.75
2	1465	35.7	1.239	33.69	65.08
			1.315	33.99	64.70
3	813	64.3	1.772	35.83	62.40
			1.795	35.86	62.35
4	409	128	2.356	38.52	59.13
			2.387	38.19	59.42
5	277	189	2.537	39.38	58.08
			2.685	39.54	57.77
6	214	244	2.798	40.48	56.73
			2.761	40.32	56.92

TABLE IV HYDROGENATION OF $SiCl_4$ AT 300 PSIG, 550°C and $H_2/SiCl_4$ RATIO OF 1.0

Experiment No.	Hydrogen Feedrate SCCM	Residence Time Second	Reaction Product Composition mole% SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	1850	12.8	0.420	21.32	78.27
			0.383	20.77	78.85
2	1157	20.5	0.702	25.90	73.40
			0.644	25.20	74.16
3	737	32.2	1.021	29.38	69.60
			0.973	29.10	69.94
4	415	57.2	1.124	30.78	68.09
			1.127	30.29	68.59
			1.117	30.28	68.61
5	222	107	1.334	33.28	65.39
			1.426	33.44	65.13

TABLE V HYDROGENATION OF $SiCl_4$ AT 300 PSIG, 500°C AND $H_2/SiCl_4$ RATIO OF 1.0

Experiment No.	Hydrogen Feedrate SCCM	Residence Time Second	Reaction Product Composition mole% SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	2606	11.7	0.090	12.84	86.26
			0.083	13.09	86.08
2	1879	16.2	0.211	16.71	83.07
			0.208	16.73	83.06
3	1288	23.6	0.351	20.39	79.26
			0.343	20.06	79.60
4	793	38.4	0.476	23.23	76.30
			0.477	23.12	76.41
5	426	71.5	0.701	25.97	73.33
			0.700	26.22	73.08
6	140	218	0.994	29.52	69.49
			1.030	29.44	69.53

TABLE VI HYDROGENATION OF $SiCl_4$ AT 300 PSIG, 450°C AND $H_2/SiCl_4$ RATIO OF 1.0

Experiment No.	Hydrogen Feedrate	Residence Time	Reaction Product Composition mole%		
	SCCM	Second	SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	2485	12.3	~0	8.166	91.84
2	1900	16.0	0.026	10.08	89.90
3	1323	23.0	0.096	12.83	87.07
4	926	32.9	0.190	16.41	83.46
5	483	63.0	0.298	19.16	80.55
6	382	79.7	0.349	20.61	79.05
7	178	171	0.609	24.47	74.93

TABLE VII HYDROGENATION OF $SiCl_4$ AT 300 PSIG 400°C AND $H_2/SiCl_4$ RATIO OF 1.0

Experiment No.	Hydrogen Feedrate	Residence Time	Reaction Product Composition mole%		
	SCCM	Second	SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	1981	15.4	~0	5.030	94.97
2	1313	23.2	~0	7.501	92.50
3	766	39.8	0.026	10.65	89.33
4	394	77.4	0.065	14.28	85.66
5	157	194	0.303	21.23	78.46

TABLE VIII HYDROGENATION OF $SiCl_4$ AT 300 PSIG, 500°C AND $H_2/SiCl_4$ RATIO OF 2.8

Experiment No.	Hydrogen Feedrate SCCM	Residence Time Second	Reaction Product Composition mole% SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	2747	17.3	0.312	20.38	79.31
2	1887	25.3	0.557	24.95	74.50
3	1545	30.8	0.711	26.79	72.50
4	1200	39.7	0.873	28.76	70.38
5	845	56.4	1.138	31.98	66.89
6	540	88.3	1.342	33.46	65.19
7	275	173	1.674	35.47	62.85

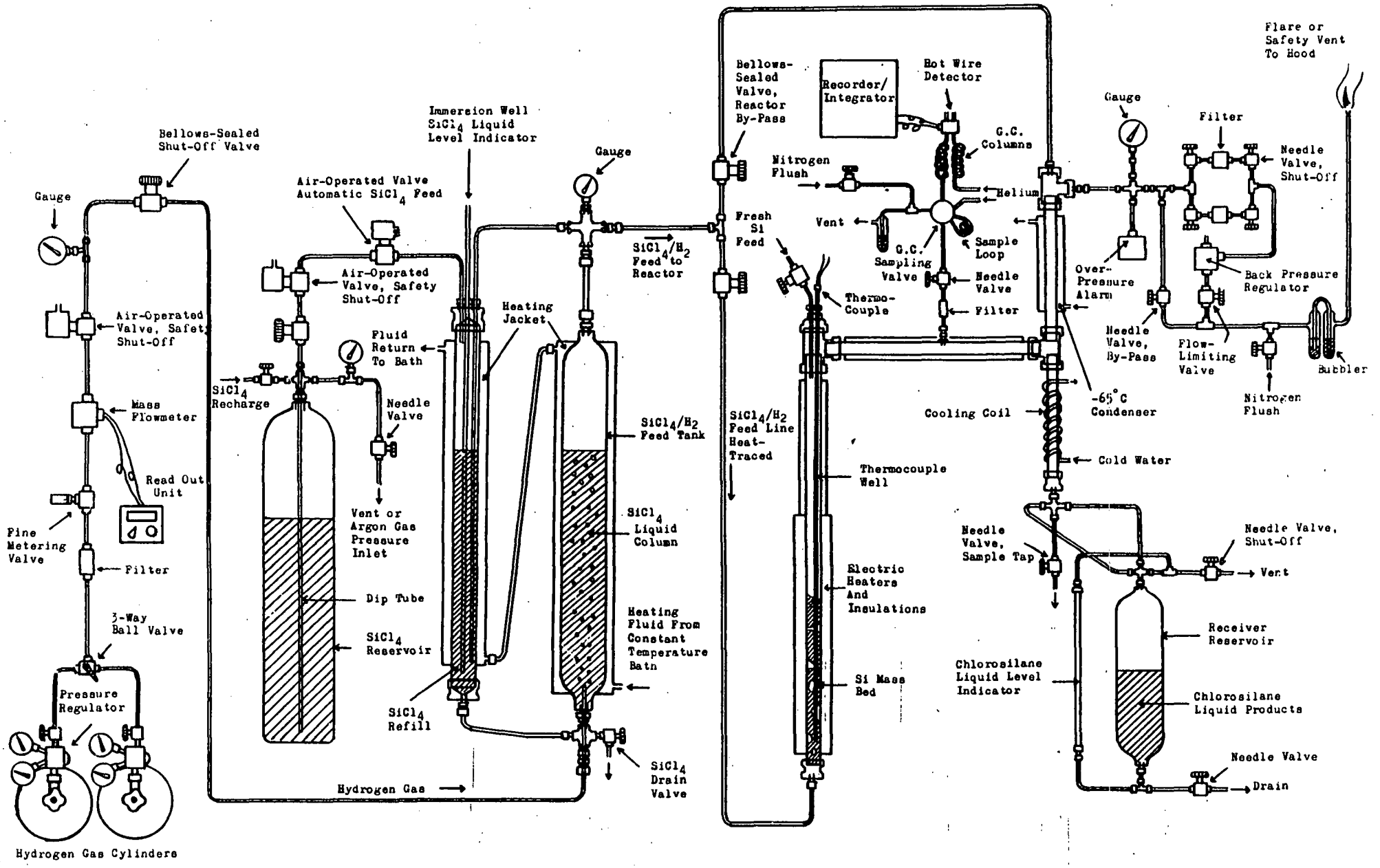
TABLE IX HYDROGENATION OF $SiCl_4$ AT 300 PSIG, 450°C AND $H_2/SiCl_4$ RATIO OF 2.8

Experiment No.	Hydrogen Feedrate	Residence Time	Reaction Product Composition mole%		
	SCCM	Second	SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	2717	19.4	0.154	15.14	84.71
2	1820	28.9	0.268	18.70	81.03
3	1273	41.3	0.403	21.97	77.63
4	884	59.5	0.541	24.72	74.75
5	680	77.4	0.650	26.70	72.64
6	455	116	0.860	28.55	70.56
7	263	200	1.070	31.32	67.61

TABLE X HYDROGENATION OF $SiCl_4$ AT 300 PSIG, 400°C AND $H_2/SiCl_4$ RATIO OF 2.8

Experiment No.	Hydrogen Feedrate SCCM	Residence Time Second	Reaction Product Composition mole% SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	2454	21.7	~0	8.519	91.48
2	1640	32.4	<0.02	12.52	87.49
3	838	63.4	0.063	14.96	84.98
4	485	110	0.324	20.41	79.27
5	219	243	0.663	25.26	74.08

FIGURE 1 Apparatus For The Hydrogenation Of $SiCl_4$ To $SiHCl_3$



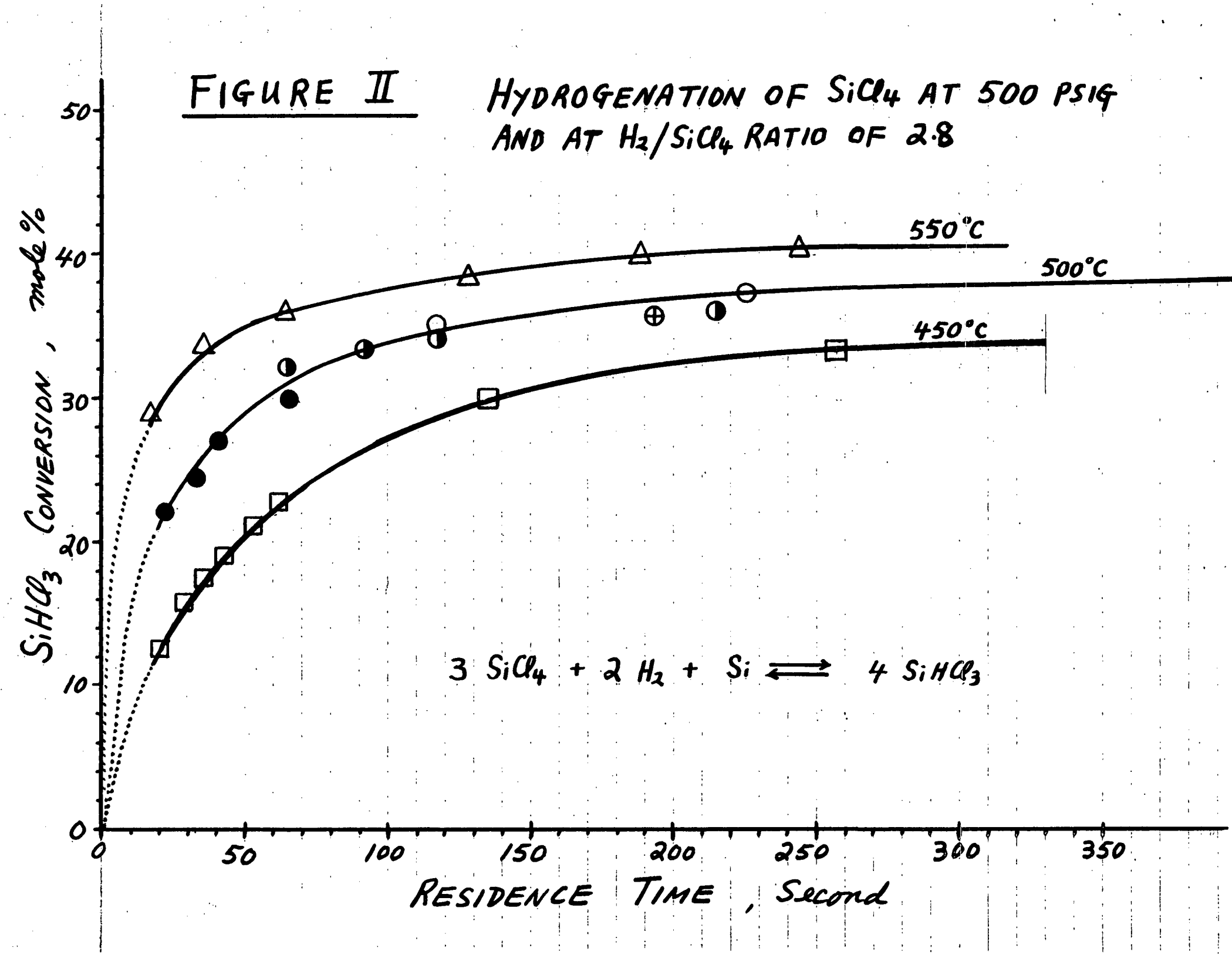


FIGURE II
HYDROGENATION OF SiCl4 AT 500 PSIG AND AT H2/SiCl4 RATIO OF 2.8
550°C
500°C
450°C
3 SiCl4 + 2 H2 + Si ⇌ 4 SiHCl3
SiHCl3 CONVERSION, mole %
RESIDENCE TIME, Second
0
10
20
30
40
50
0
50
100
150
200
250
300
350

FIGURE III HYDROGENATION OF $SiCl_4$ AT 300 PSIG AND $H_2/SiCl_4$ RATIO OF 1.0

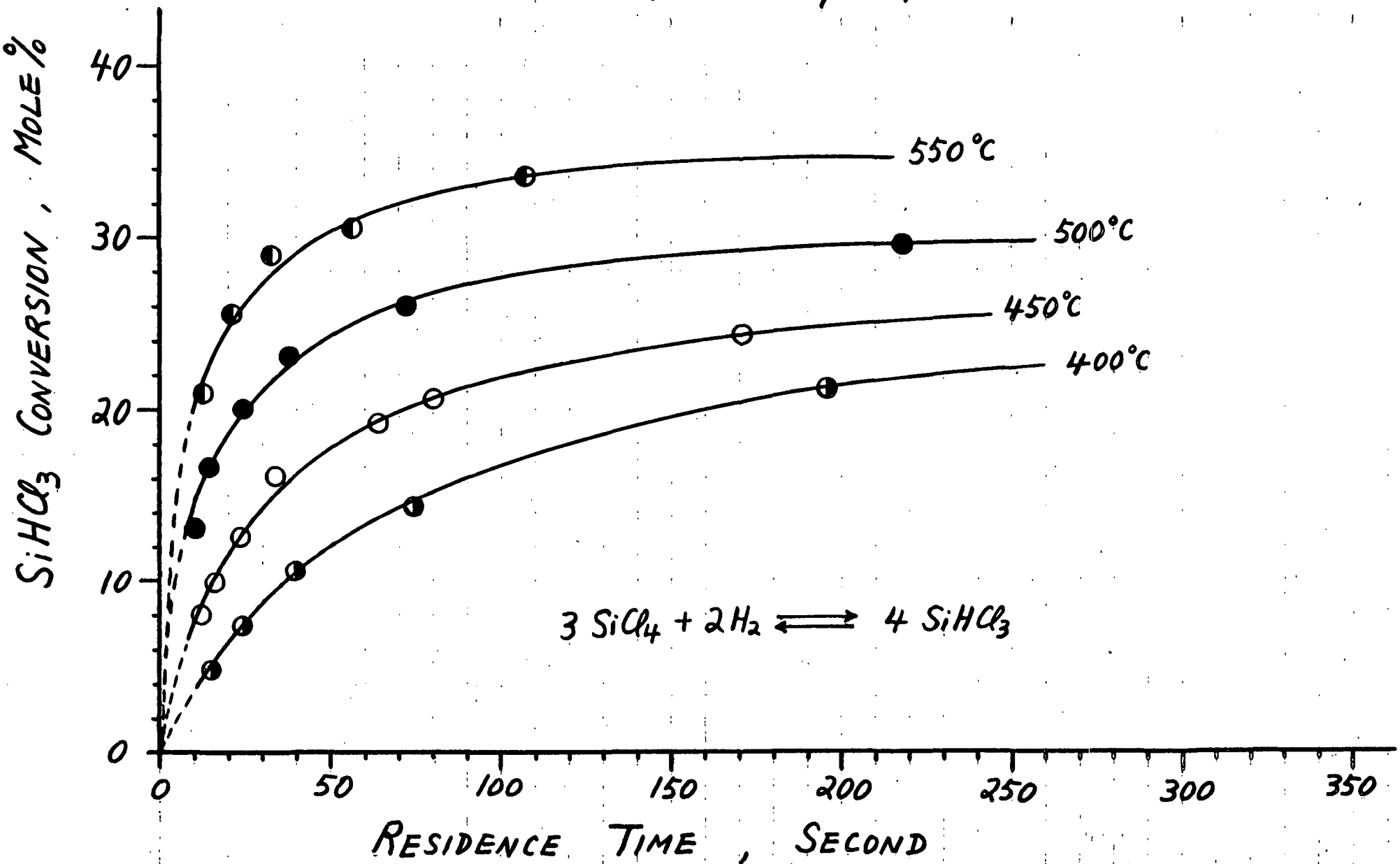


FIGURE IV

HYDROGENATION OF $SiCl_4$ AT 300 PSIG AND $H_2/SiCl_4$ RATIO OF 2.8

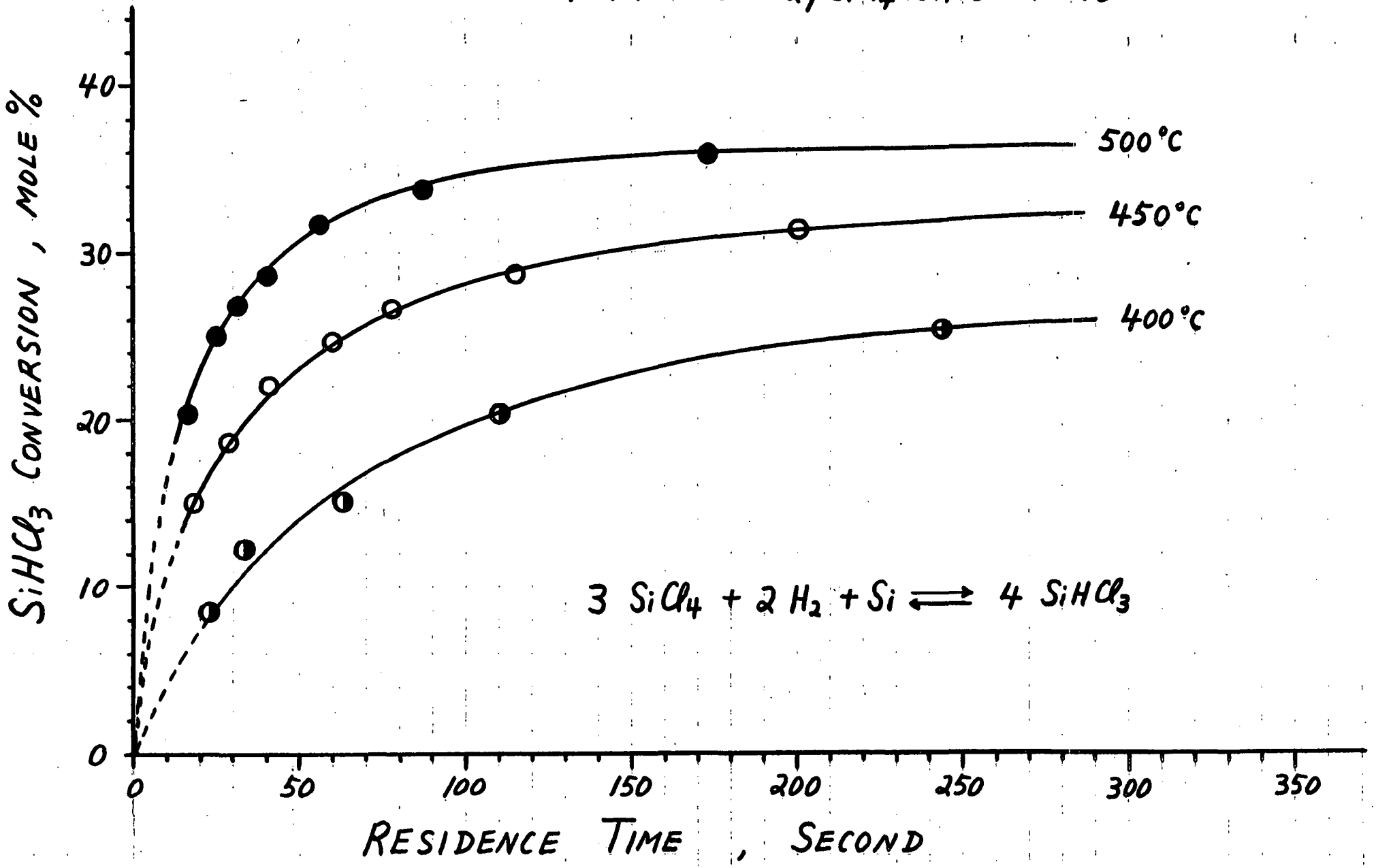


FIGURE V EFFECT OF $H_2 : SiCl_4$ RATIO ON THE HYDROGENATION OF $SiCl_4$ AT 500°C, 300 PSIG

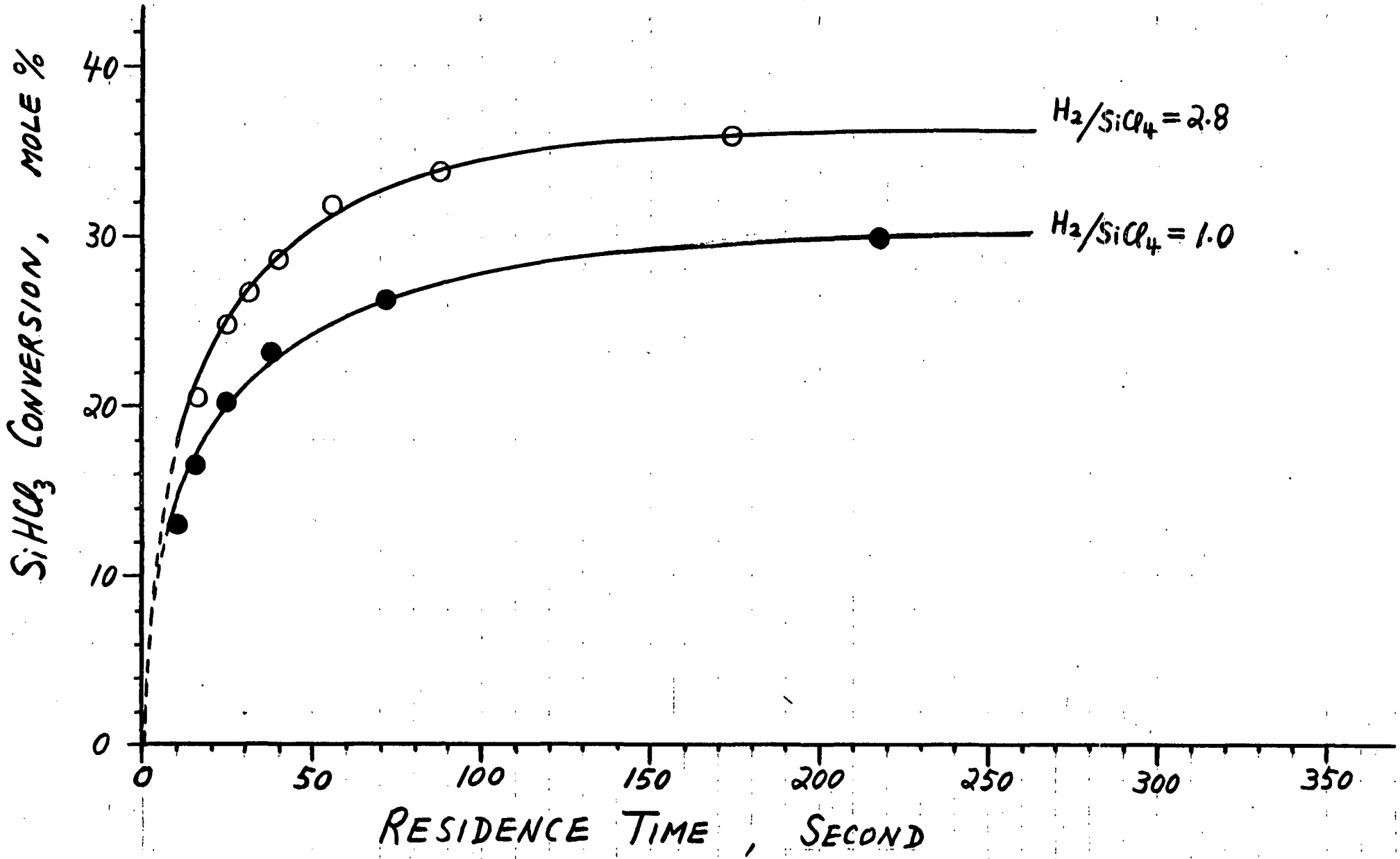


FIGURE VI

EFFECT OF PRESSURE ON THE REACTION RATE AT 450 °C, $H_2/SiCl_4$ RATIO OF 2.8

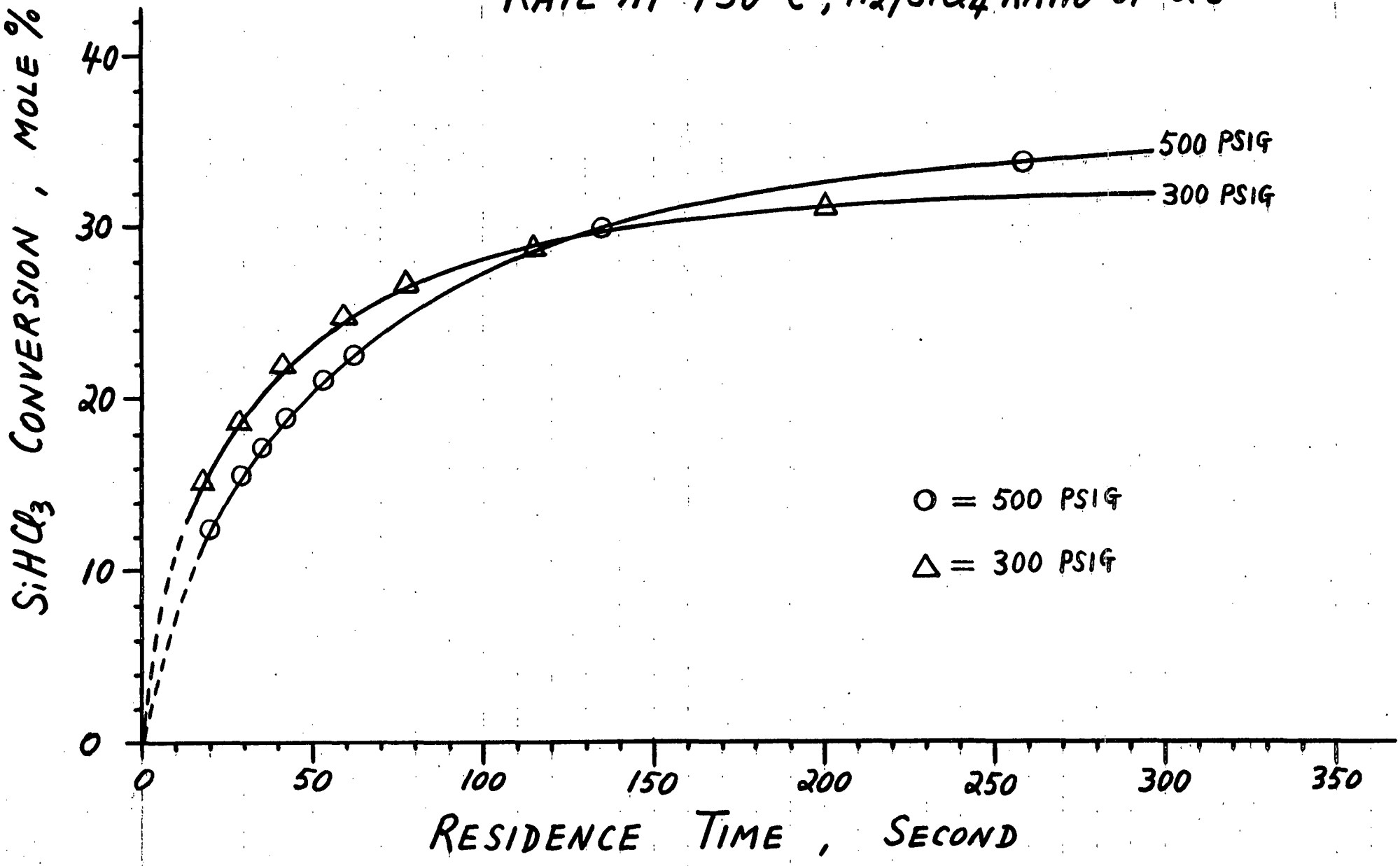


FIGURE VII EFFECT OF PRESSURE ON THE REACTION RATE AT 500°C, $H_2/SiCl_4$ RATIO OF 2.8

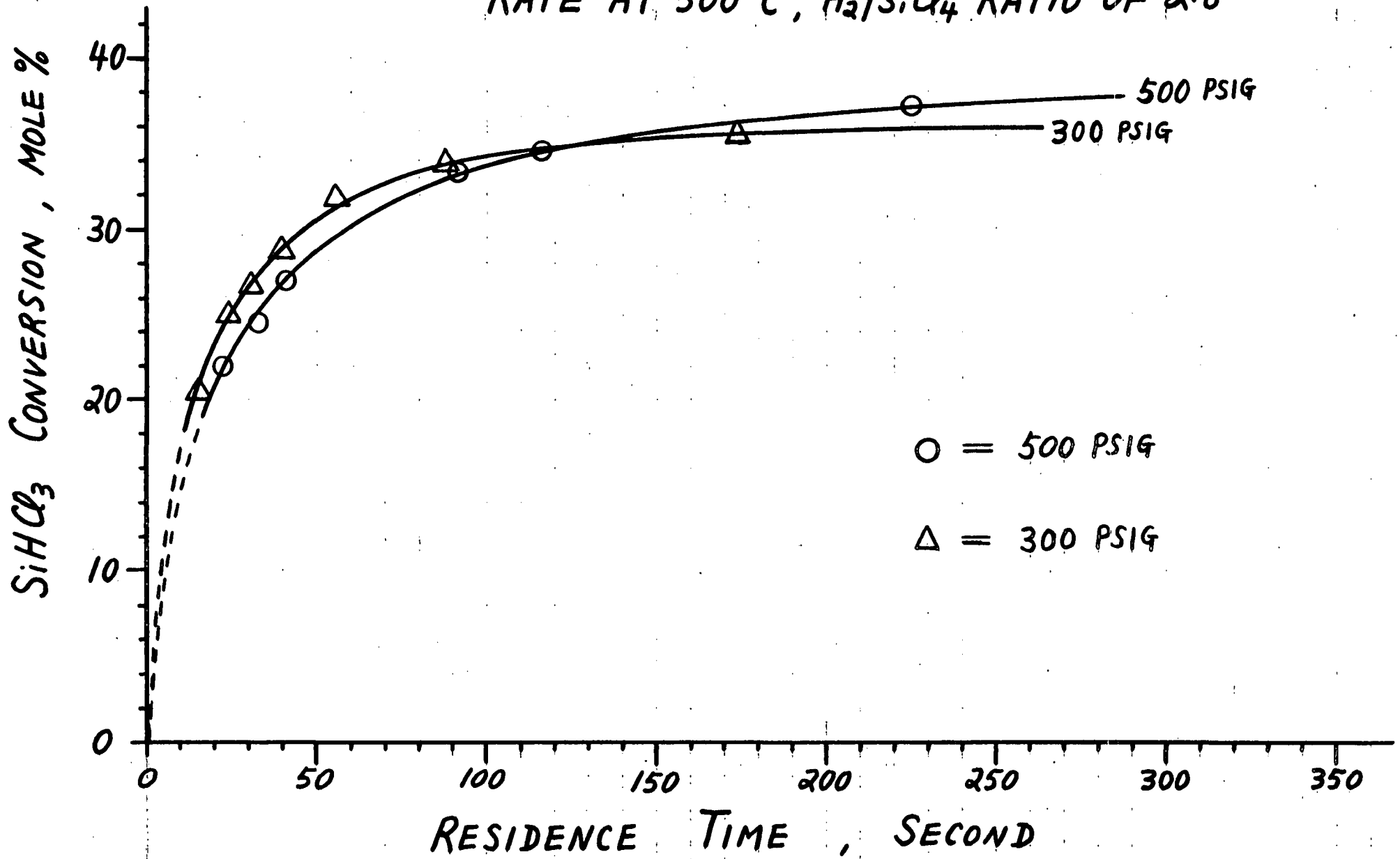
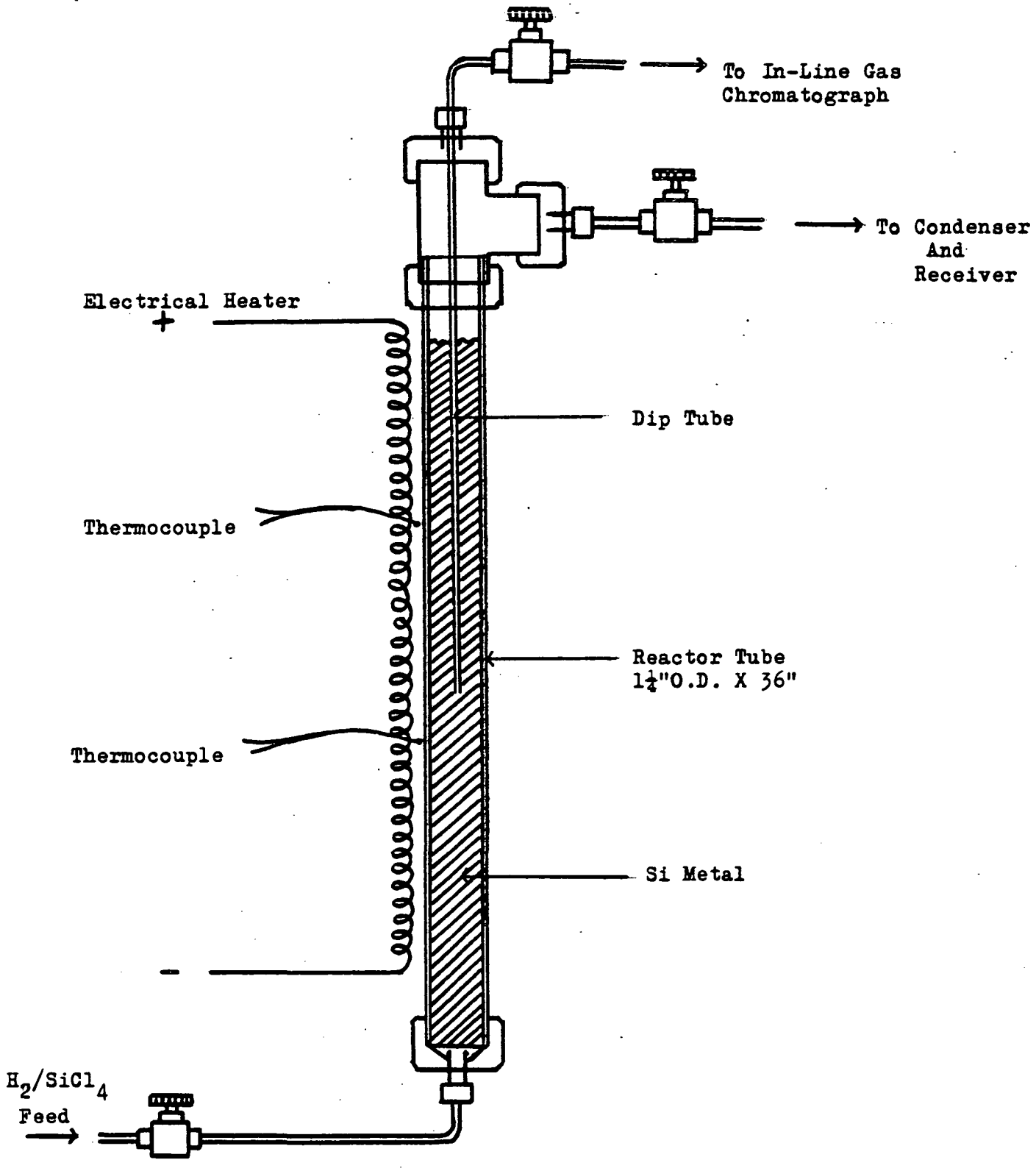


FIGURE VIII SEALED, STATIC BED REACTOR FOR EQUILIBRIUM MEASUREMENTS



PROGRAM PLAN Investigation of the Hydrogenation of $SiCl_4$ (JPL Contract No. 955582)

	1979									1980												1981		
Year / Month of Year	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3
Month of Contract	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
I Program Plan, Laboratory Site Preparation	~~1~~																							
II Finalize Reactor Design, Order Equipment	~~1~~	~~2~~																						
III Construct Hydrogenation Apparatus		~~2~~	~~3~~	~~4~~	~~5~~																			
IV Safety Review, Start-Up, Standardization					~~5~~																			
V Process Studies								▲						▲				▲						
A. Reaction Kinetics																								
(1) Function of T,P,$H_2/SiCl_4$: with no Catalyst					~~5~~	~~6~~	~~7~~	~~8~~																
(2) Establish Rate Equation, Reaction Order								~~8~~	~~9~~	10	11													
(3) Copper Catalyst Studies: T,P,$H_2/SiCl_4$								~~8~~	~~9~~	10	11	12	13											
(4) Particle Size Distribution, Surface Area													13	14	15									
(5) Different Grade of MG Si														14	15	16								
B. Mass Life Studies																								
(1) With no Catalyst Added																	16	17	18					
(2) With Cu Catalyst Added																			18	19	20			
(3) Different Grade of MG Si																					20	21	22	
VI Research and Development								▲						▲				▲						
A. Method of Preparing Cu/Si Mass																								
(1) Literature Studies	~~1~~	~~2~~	~~3~~	~~4~~	~~5~~	~~6~~	~~7~~	~~8~~																
(2) Prepare Cu/Si Mass					~~5~~	~~6~~	~~7~~	~~8~~																
(3) Evaluation and Optimization								~~8~~	~~9~~	10	11	12	13											
B. Reaction Mechanism Studies																								
(1) Literature Studies	~~1~~	~~2~~	~~3~~	~~4~~	~~5~~	~~6~~	~~7~~	~~8~~																
(2) Identify Reaction Intermediates: HCl, etc.						~~6~~	~~7~~	~~8~~	~~9~~	10	11	12	13	14	15	16	17	18	19	20	21			
(3) Identify Intermediate Reaction Steps						~~6~~	~~7~~	~~8~~	~~9~~	10	11	12	13	14	15	16	17	18	19	20	21			
(4) Nature of the Equilibrium Reactions						~~6~~	~~7~~	~~8~~	~~9~~	10	11	12	13	14	15	16	17	18	19	20	21			
(5) The Role of Copper Catalyst																								
a. Nature of the Catalytic Sites								~~8~~	~~9~~	10	11	12	13	14	15									
b. Copper Transport Mechanism								~~8~~	~~9~~	10	11	12	13	14	15									
c. Copper Distribution on Solid Si Surfaces								~~8~~	~~9~~	10	11	12	13	14	15									
(6) Kinetic Isotope Effect													▲									22	23	
C. Other Hydrogenation Catalysts													▲									22	23	
VII Reports																								
A. Recomendation on Optimun Reaction Conditions									~~9~~					14					19				23	
B. Recomendation for Additional Development Work									~~9~~					14									23	
C. Final Report																							23	24

▲ Milestone Check Points